

Coexistence of Magnetism and Superconductivity in the Iron-based Compound $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$

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We report on muon-spin rotation and relaxation (μSR), electrical resistivity, magnetization and differential scanning calorimetry measurements performed on a high-quality single crystal of $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$. Whereas our transport and magnetization data confirm the bulk character of the superconducting state below $T_c = 29.6(2)$ K, the μSR data indicate that the system is *magnetic* below $T_N = 478.5(3)$ K, where a first-order transition occurs. The first-order character of the magnetic transition is confirmed by differential scanning calorimetry data. Taken all together, these data indicate in $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ a microscopic coexistence between the superconducting phase and a strong magnetic phase. The observed T_N is the highest reported to date for a magnetic superconductor.

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The discovery of superconductivity in the Fe-based systems has triggered a remarkable renewed interest for possible new routes leading to high- T_c superconductivity [1]. As observed in the cuprates, the iron-based superconductors, exhibit an interplay between magnetism and superconductivity suggesting the possible occurrence of unconventional superconducting states. Other common properties are the layered structure and the low carrier density. A result of the numerous studies on iron-based systems has been the discovery of a series of superconducting material based on FeAs-layer, as the so-called ‘1111’ ($\text{ReFeAsO}_{1-x}\text{F}_x$, Re = rare-earth), the ‘111’ (LiFeAs), the ‘122’ AFe_2As_2 ($\text{A} = \text{K}, \text{Sr}, \text{Ba}$) or the ‘22426’ ($\text{Fe}_2\text{As}_2\text{Ae}_4\text{M}_2\text{O}_6$ where Ae is an alkaline earth metal and M is a transition metal) families (for review see, *e.g.*, Ref. 2 and references therein).

Besides FeAs-layer systems, superconductivity has been reported in the related compound FeSe_{1-x} (‘11’ or ‘011’ family) [3]. This system presents a remarkable increase of T_c under pressure or by a partial substitution on the chalcogenide site. In addition, recent muon-spin rotation and relaxation (μSR) and magnetization studies, performed by some of us [4], have revealed the occurrence of antiferromagnetism under pressure (above ~ 0.8 GPa) and its coexistence with superconductivity on short length scales in the full sample volume. Furthermore, both forms of order appear to be stabilized by pressure, since T_c as well as T_N and the magnetic order parameter simultaneously increase with increasing pressure. All these results establish that FeSe-layer systems are themselves remarkable superconductors and call for the further study of new FeSe-based superconductor families.

Very recently superconductivity at about 30 K was reported in the FeSe-layer compound $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ (see Ref. 5). This compound was obtained by solid state

reaction leading to a potassium intercalation between FeSe layers. This system is isostructural to the ‘122’ (i.e. tetragonal ThCr_2Si_2 type structure – space group $I4/mmm$). Soon after, some of us discovered that the related compound $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ exhibits a similar superconducting transition temperature ($T_c \simeq 27.4$ K) [6]. It was shown, in addition, that rather large single crystals of $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ can be produced, allowing one to hopefully performed a full study of the microscopic superconducting and/or magnetic properties.

These recent discoveries allow one to perform a direct comparison between both families of the chalcogenide-‘122’ and pnictide-‘122’ systems concerning the interplay between magnetism and superconductivity. In the pnictide-‘122’ there is an ongoing debate about the kind of coexistence of magnetism and superconductivity in the under-doped region of the phase diagram. In the alkali-metal ion substituted systems, magnetism and superconductivity seem to compete since they only coexist in a phase separated manner [7]. On the other side, when doped on the Fe site the pnictide-‘122’ systems apparently show a microscopic coexistence as evidenced by NMR measurements [8]. Anyhow a competition between the two forms of order in the latter case is apparent from neutron scattering works since the magnetic order parameter is partially suppressed below the superconducting transition temperature [9, 10]. Hence, it appears that in the pnictide-‘122’ systems static magnetism has to be destroyed by a control parameter like doping or pressure before superconductivity can develop its full strength.

Here we report on μSR , transport and thermodynamic measurements on $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ which demonstrate the occurrence of both static magnetism and superconductivity in this system. Our measurements unambiguously show that both states microscopically coexist at low temperatures. Surprisingly, we find magnetic ordering with

an unexpectedly high Néel temperature of ~ 478 K and at the same time a high superconducting $T_c \simeq 30$ K showing that both order parameters are quite robust and may coexist without apparent competition.

A single crystal of $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ was grown from the melt using the Bridgman method [6]. From this large single crystal, different samples were obtained by cleaving the crystal along the basal plane of the tetragonal structure. No significant deviation could be observed on the physical properties of the different samples. They were characterized by powder x-ray diffraction using a D8 Advance Bruker AXS diffractometer with $\text{Cu } K_\alpha$ radiation. The magnetic properties of the crystals were investigated by a commercial *Quantum Design* 7 T Magnetic Property Measurement System MPMS-XL SQUID Magnetometer at temperatures ranging from 2 K to 50 K using the Reciprocating Sample Option. The measurements of resistivity were done using the *Quantum Design* Physical Properties Measurement System PPMS-9 in a temperature range from 2 K to 300 K. Differential scanning calorimetry (DSC) experiments were performed with a Netzsch DSC 204F1 system. Measurements were performed on heating and cooling with a rate of 5-20 K/min using 20 mg samples encapsulated in standard Al crucibles. An argon stream was used during the whole experiment as protecting gas. Finally, zero-field and transverse-field μSR data were obtained using the GPS and DOLLY instruments located on the πM3 and πE1 beamlines of the Swiss Muon Source (Paul Scherrer Institute Villigen, Switzerland). Measurements were performed with static and dynamical helium flow cryostats between 2 and 315 K and with a Janis closed-cycle refrigerator between 300 and 500 K.

The first step of our investigation was to confirm the superconducting ground state of $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$. This was performed by measuring the electrical resistivity and magnetization. As shown on Fig. 1, these data confirm the occurrence and bulk character of the superconducting state below $T_c \simeq 29.6$ K. The resistivity was measured with the electrical current applied in the basal plane. The magnetization data were obtained in a magnetic field of $\mu_0 H = 30 \mu\text{T}$ with the crystallographic c -axis parallel to the field. For the adopted geometry during our magnetization measurements, the demagnetization factor N of our sample (dimensions: $2 \times 3.8 \times 2 \text{ mm}^3$) was estimated to be 0.44 (see, *e.g.*, Ref. 11) which leads to a superconducting volume fraction compatible with 100% of the sample volume.

With this in mind, we turned our focus on the determination of the microscopic properties by μSR , performing first zero-field experiments. Generally, the zero-field μSR signal for a single crystal can be written as [12]:

$$A(t) = A_0 \int f(\mathbf{B}_\mu) \left[\cos^2 \theta + \sin^2 \theta \cos(\gamma_\mu B_\mu t) \right] d\mathbf{B}_\mu, \quad (1)$$

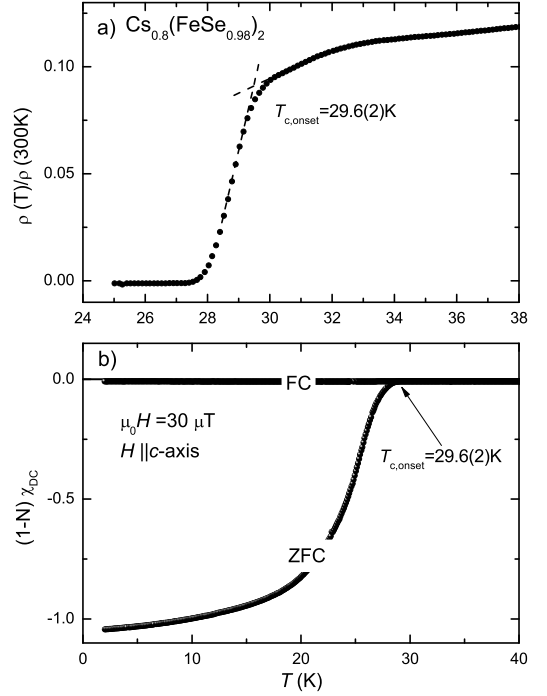


FIG. 1: a) Temperature dependence of the electrical resistivity of $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ in the vicinity of the superconducting transition. b) Temperature dependence of dc magnetic susceptibility for both zero-field cooling (ZFC) and field cooling procedures (FC) obtained with a magnetic field of $\mu_0 H = 30 \mu\text{T}$ applied along the c -axis.

where A_0 is the initial asymmetry, $f(\mathbf{B}_\mu)$ is the magnetic field distribution function at the muon site, θ is the angle between the local internal field and the initial muon-spin polarization $\mathbf{P}_\mu(0)$, and $\gamma_\mu/(2\pi)$ is the gyromagnetic ratio of the muon. Surprisingly, as shown on Fig. 2, it appeared that at low temperatures essentially the full μSR signal arising from the sample (more precisely about 95% of it) is wiped out when performing zero-field μSR measurements with $\mathbf{P}_\mu(0)$ oriented along the crystallographic basal plane. On the other hand, a full and non-depolarizing signal is obtained when the initial polarization is parallel to the c -axis. Therefore, our observations show that the muon is sensing *spontaneous static internal fields* \mathbf{B}_μ at low temperatures oriented solely along the c -axis. Such behavior is only observed in long range ordered magnetic materials with a well defined internal-field direction at the muon site. It also indicates an homogeneous magnetic state without contributions of magnetic impurity phases (possessing different magnetic structures). In addition, the absence of a detectable μSR signal when $\mathbf{P}_\mu(0) \perp \hat{\mathbf{c}}$ [i.e. $\mathbf{P}_\mu(0) \perp \mathbf{B}_\mu$] indicates either a very high value of the internal field (leading to muon spin precessions much faster than our time resolution) or more probably a large field distribution along the c -axis due to a complicated magnetic structure with possible large or spatially modulated ordered moments.

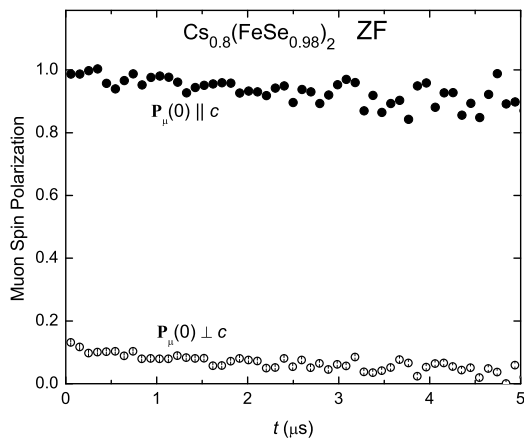


FIG. 2: μ SR signals recorded at 2 K with the initial muon polarization along and perpendicular to the crystallographic c -axis. About a fraction of 0.07 of the signal is due to the cryostat and sample holder signal which is slowly relaxing. Note the missing amplitude for the geometry corresponding to the initial muon polarization perpendicular to the c -axis.

Note that neutron scattering measurements [13] yield an ordered moment of $\approx 2 \mu_B$ in the related chalcogenide FeTe in which a well defined, albeit strongly damped, μ SR precession is observed [14]. This suggests that the ordered magnetic moment in $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ is at least of the order of $2 \mu_B$ also.

It should be stressed that the static, most probably antiferromagnetic order persists down to 2 K, i.e. well into the superconducting state. This is especially noteworthy as a part of the very same crystal which was studied in the magnetization experiment discussed above is found to exhibit bulk superconductivity (see Fig. 1 b). Therefore, the μ SR data unambiguously indicate a *microscopic coexistence between magnetism and superconductivity*.

To gain more insight on the magnetic state, we performed zero-field as well as weak-transverse-field (WTF) μ SR measurements up to 500 K. μ SR measurements in the WTF configuration are used to determine the volume fractions of sample regions with and without static magnetic order. A persistent oscillation amplitude in WTF μ SR spectra would reflect the fraction of the muons ensemble (i.e. fraction of the sample volume) with a non-magnetic environment. Figure 3 shows the precessing amplitude of the obtained WTF μ SR signal normalized to its value obtained in the paramagnetic state. Up to about 475 K, the μ SR amplitude is very low, indicating that $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ is still in a magnetic state. Upon increasing the sample temperature above 479 K, a step-like increase of the WTF μ SR amplitude is observed indicating the transition to a paramagnetic state at higher temperature [15]. The fact that the whole sample orders at a well defined ordering temperature again proves the homogeneity of our sample and excludes possible impurity phases to be present. The ordering tempera-

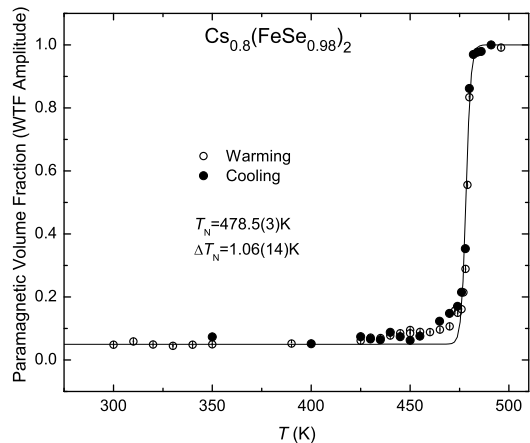


FIG. 3: Amplitude of the persisting precession obtained in WTF μ SR experiments ($\mu_0 H = 3$ mT) in $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$. Such amplitude represents the paramagnetic volume fraction of the sample as it corresponds to the fraction of muons stopping in a nonmagnetic environment. The solid line is the fit by using a Fermi-type function (see text for details). Note the step-like behavior at $T \simeq 479$ K. No clear hysteresis could be observed upon cooling and warming.

ture T_N was determined by fitting a Fermi-type function: $\{1 + \exp[(T_N - T)/\Delta T_N]\}^{-1}$ (ΔT_N is the width of transition) to the data (solid line in Fig. 3) [16]. The sharpness of the transition [$\Delta T_N = 1.06(14)$ K] is compatible with a first-order transition as confirmed further by our DSC data (see below). The very high magnetic transition temperature [$T_N = 478.5(3)$ K, $T_N \simeq 17 \times T_c$] and the possibly high value of the ordered moments, as also confirmed by the first-principles calculations [17, 18], indicate a very robust magnetic state. The observation of a microscopic coexistence between this strong magnetic state and superconductivity at low temperatures is rather astonishing and points to an unconventional character for the superconducting state. Note that the observed T_N is, to the best of our knowledge, the highest reported so far for any kind of magnetic superconductor.

The first-order type of the magnetic transition at $T_N = 478.5(3)$ K is confirmed by our DSC measurements reported in Fig. 4. A small but definite peak is observed in the data reflecting an enthalpy of transition due to the first order magnetic transition. The temperature onset is of the order of 477 K, i.e. perfectly compatible with what observed in the μ SR data. The small difference might arise from an imperfect sample thermalization in the rather fast cooled DSC measurements. We observe a slight temperature hysteresis between the DSC data obtained upon warming (not shown) and cooling which also seems dependent on the temperature sweep rate used during the measurements. As DSC measurements have to be performed with a finite temperature sweeping rate, no real conclusions can be drawn about a possible temperature hysteresis. On the other hand, our WTF μ SR

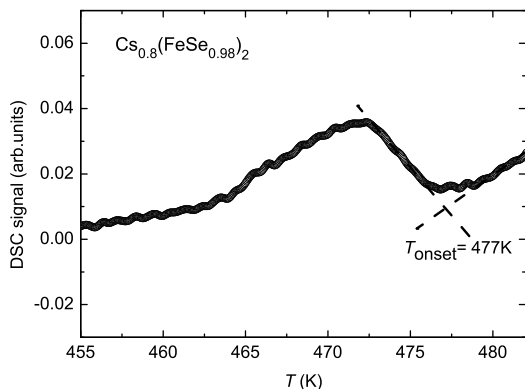


FIG. 4: Differential scanning calorimetry (DSC) signal recorded upon cooling with a sweeping rate of 20 K/min in $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$. The small but clear peak, with an onset temperature of ~ 477 K signals an enthalpy of transition ΔH characterizing a first-order transition.

data do not show a visible temperature hysteresis around the transition at $T_N \simeq 479$ K.

As said above, the observation of coexistence of magnetism and superconductivity has already been reported in pnictides-‘122’ [7, 19, 20]. A characteristic of these iron-based family is that the temperature of the magnetic transition needs to decrease (by doping or external pressure) prior to observe a superconducting state at low temperature. Moreover, the ratio between T_N and T_c is always much smaller for samples with T_c near to the optimum than that observed in our present measurements for $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$. In addition T_c is always found to increase upon decreasing the strength of the magnetic state. Therefore, it could appear very appealing to try to weaken the magnetic state in $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ in order to strengthen the superconducting state (i.e. increase T_c). Obviously, additional measurements tracking the evolution of both transitions as a function of doping and/or pressure are urgently needed.

On the other hand, the interplay between magnetism and superconductivity in the chalcogenide iron-based systems might be rather opposite than the one observed in the pnictides. An unusual behavior has been observed in the FeSe_{1-x} family under pressure [4]. By applying pressures above 0.8 GPa a static magnetic phase appears which microscopically coexists with superconductivity. In addition, one observes that *both* the magnetic [4] and superconducting [4, 21] transition temperatures increase with increasing pressure. In this vein, we note that the pressure evolution of T_c in FeSe_{1-x} appears first to saturate in the absence of magnetic state. The subsequent strong increase of T_c , observed upon increasing the pressure above 0.8 GPa, is concomitant to the occurrence of static magnetism increasing under pressure. It

is therefore plausible to consider that a strong magnetic state might be even the prerequisite for the observation of high- T_c ’s in chalcogenide iron-based systems.

In summary, we have presented strong evidence that the superconducting state observed in $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ below 29.6(2) K is actually microscopically coexisting with a rather strong magnetic phase with a transition temperature at 478.5(3) K. DSC data point to a first-order character for the magnetic transition, which appears characterized by rather large static iron-moments as the μSR signal is wiped out for an initial muon-polarization perpendicular to the crystallographic c -axis.

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